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LAND TREATMENT FIELD STUDIES

Volume 2. Oily Waste from a Petroleum Refinery

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FOREWORD

The U.S. Environmental Protection Agency was created because of increasing public and government concern about the dangers of pollution to the health and welfare of the American people. Noxious air, foul water, and spoiled land are tragic testimonies to the deterioration of our natural environment. The complexity of that environment and the interplay of its components require a concentrated and integrated attack on the problem.

Research and development is that necessary first step in problem solution; and it involves defining the problem, measuring its impact, and searching for solutions. The Municipal Environmental Research Laboratory develops new and improved technology and systems to prevent, treat, and manage wastewater and solid and hazardous waste pollutant discharges from municipal and community sources, to preserve and treat public drinking water supplies, and to minimize the adverse economic, social, health, and aesthetic effects of pollution. This publication is one of the products of that research and provides a most vital communications link between the researcher and the user community.

This report provides the results of a field study investigation of one of six sites receiving industrial waste sludges by land cultivation. The purpose of the study was to identify and verify parameters which lead to environmental acceptability of the waste, and to recommend research needs for establishing guidelines and criteria for land cultivation.

Francis T. Mayo, Director
Municipal Environmental Research
Laboratory

ABSTRACT

This report presents the results of field measurements and observations of a land treatment site operated for disposal of petroleum refinery waste sludges. The waste, principally API separator bottoms, was land treated in an area long used for waste disposal. The site was sampled once, and observations were made on the type and amount of waste handled, site characteristics, and management procedures for waste application and monitoring. Organic and inorganic analyses were conducted on the waste and soil/waste mixture; inorganic analysis was performed on plant samples.

The site is a portion of man-made fill bordered by an estuary, wastewater lagoon, and heavily industrialized land. The geophysical characteristics of the site (topography, meteorology, hydrology, etc.) make contamination of the surrounding environment unlikely, except possibly in the event of an unusually severe storm.

This site receives large quantities of waste--on the order of 5.75 million gallons per year. The land treatment site management operated the site in accordance with state permit requirements. Treated plots of land are aerated monthly and monitoring occurs frequently. However, the monitoring results are not used as the basis for the rate and quantity of further waste applications.

The results of soil analysis indicated that the waste on the site was not undergoing optimal degradation because of the heavy loading. Accumulation of heavy metals and organic compounds was observed in the top 12" of soil. Further research should be directed at monitoring the rate of degradation of these wastes by reducing the loading rate on the site and by using fertilizer to create a better nitrogen to carbon ratio for degradation.

This report was submitted in fulfillment of Contract No. 68-03-2602 by Arthur D. Little, Inc., under sponsorship of the U.S. Environmental Protection Agency. This report covers the period September 1977 through February 1981 and work was completed in May 1981.

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SECTION 1

INTRODUCTION

Land treatment is the application and incorporation of solid or semi-solid waste into surficial soils. Other terms used to describe this practice include landfarming, land cultivation, refuse farming, land spreading, soil farming and soil incorporation. The term land application, on the other hand, usually refers to irrigation of surficial soil with wastewater. Land treatment is essentially a physical/chemical/biological waste treatment method that utilizes the natural capacity of the soil system to aerobically degrade, assimilate and immobilize certain waste constituents.

At every land treatment site, there is a dynamic balance of decomposition, attenuation and migration of waste constituents. The extent ot which any one of these mechanisms occurs depends on the waste character, site character and cultivation procedures.

A land treatment site should provide decomposition of the organic constituents applied and incorporated. The migration of soluble constituents from a land treatment site should be within environmentally acceptable concentrations for the receiving media, particularly ground and surface waters. The attenuation of remaining constituents over the design life of the site should not lead to a build up of total concentrations that could harm the soil structure, cause phytotoxicity, or lead to excessive concentrations in the food web through bioaccumulation.

From the above discussion, it is evident that specific site characteristics and waste characteristics together are key to achieving environmentally optimal use of surficial soils in waste treatment. Equally important (although not as evident) is the management of the land cultivation operation; no matter how optimal conditions may be for degradation/attenuation of waste, some sites can be overloaded. Management of a site can be viewed as the means through which desired waste treatment conditions are maintained.

OBJECTIVES

The obejctive of this project was to identify parameters which contribute to (or affect) the environmental acceptability of land treatment for the sludge waste from a petroleum refinery plant. The parameters are classified by waste characteristics (e.g., percent solids, salt content), site characteristics (e.g., topography, climate) and landtreatment management procedures (e.g., soil aeration, frequency of waste application). Environmental

acceptability was determined by comparison of the concentrations of waste constituents in application area soils with those in control area soils, and by evaluation of the potential for environmental contamination.

DESCRIPTION OF THE SITE

The identity of this site is protected by a confidentiality agreement included as part of the contract for this study. It is a "captive" site for refinery wastes located in the southern United States.

Waste Characteristics

Land treatment has been a disposal option utilized by the petroleum refining industry for years, a fact which influenced the management of this site to choose this disposal method. A number of different oily wastes are landfarmed at this site, of which the majority (90%) originate from oil/water API separator bottom sludges. Prior to disposal, the sludge bottoms are pumped through two settling ponds in series with a detention time of 2-4 weeks. The 5-7.5 million gallons of settled sludge landfarmed per year (13,700-20,500 gallons/day) are composed of 34% solids, 11% oil, and 55% water as spread.

Site Characteristics

This 20-acre site is located in a large, heavily industrialized complex on a spit of land bounded on the east by a wastewater lagoon, and on the west by a ship channel. Neighboring land is also used for heavy industry. The actual site had once been wetland, and over the years had been filled in with dredge spoils and spoils from construction and earthmoving activities. The odor of refinery products is obvious at the site, as it is in the industrial complex as a whole.

Table 1 details reported and observed site characteristics. The soil at this site is difficult to characterize because of the highly variable properties associated with man-made soils. The site personnel reported that the principal source of fill for this area was dredge spoils, which may have soil characteristics similar to those of bay margins and delta fronts. Delta soils are predominantly clay like sand and silt. If this is true, the soils should be characterized by fairly low permeability and moderate water holding capacity. Site personnel have indicated that the disposal site is underlain by a minimum of 430 cm of clay with a permeability on the order of 1.0×10^{-7} cm/sec. Given these conditions, and the high cation exchange capacity (CEC) and alkaline pH of the soil, the site should achieve good attenuation of heavy metals.

The proximity of surface waters and the low-level topography at the site make direct contact of water with the waste a possibility. Although very high berms have been constructed, an extreme storm event could cause flooding and washout, thereby introducing contaminants to the bay and nearby wastewater lagoon. The site is graded to direct runoff to the lagoon. Since the land treatment area is surrounded by heavily developed

TABLE 1. SELECTED PHYSICAL/CHEMICAL CHARACTERISTICS OF THE SITE

Characteristics	Published Source*	Data From Site Visit/ Analysis**
I. Soil		
A. Soil Classification	Man-made	Man-made: - dredge spoil - construction fill
B. pH Characteristics	-	7.8 to 8.0 (control area
C. Cation Exchange Capacity (meq/100g soil)	-	22.9 to 31.7 meq/100g (control area)
D. Soil Organic Content	-	TOC:0.78% dry solids (control area)
E. Water Retention Ability	-	-
II. Ground & Surface Water Proximity		
A. Surface Water	33M on west	17M on east (waste-water lagoon) 33M on west (bay)
B. Ground Water	-	-
III. Topographic Conditions		
A. General Topography of Vicinity of Site	Level man-made area.	-
B. Topographic Relief of Area Visited	-	Flat; subsidence in area significant.
IV. Meteorological Conditions		
A. Yearly average precipitation	cm 122	
B. Distribution of precipitation	Fairly even	
C. Frost Free Period	Essentially frost free	
D. Average maximum temperatures (°C)		
Summer	34	
Winter	6	

*Includes information from Soil Conservation Service Personnel & Publications, USGS Surveys and/or State & University Surveys.

**Includes Arthur D. Little, Inc. observations and analyses from site visits, as well as interviews with facility personnel and representatives of waste generators and farms.

land or water, the fauna that utilize the area are largely restricted to migratory birds. Species actually observed near the site were rabbits, lizards, two types of birds (killdeer and sparrow) and a variety of invertebrates were noticed on the site itself. A greater variety of aquatic birds was observed in the lagoons and bay adjacent to the site. Finfish and shellfish of commercial and recreational importance in the estuary should not be exposed to waste from the site except via possible leaching or as a result of a major storm event. Thus the wildlife exposed to the greatest concentration of waste are those utilizing the wastewater lagoon which receives runoff from the site.

Landfarm Management

The waste is generated half a mile from the site which is a part of the industrial complex. With the exception of a hauler contracted to transport the waste, all personnel in the land treatment operation are employees of the waste generator (Table 2). The waste generator has assigned one employee three-quarters time to operate the land treatment operation, and supplemental professional support, also at three-quarters time.

Typically, vacuum trucks (10-20 cubic yard capacity) from one of a number of contract haulers are used to transport the waste. During the winter of 1977-78, a second method of waste transport was tried -- a pipe line for the dredged sludge. This method required addition of water at the pond and removal of water at the land treatment site. The water operator has not determined which is the optimum method of transport.

According to site personnel, each area of the land treatment site receives waste once per year. Essentially, the application and incorporation procedures followed at this site are those agreed upon in the waste disposal permit filed with the state regulatory authorities.

Once the vacuum truck dumps the sludge at the edge of the land treatment area, site personnel spread the waste using a bulldozer dragging three telephone poles. The procedure results in somewhat uneven application, but on the average, the waste is spread three or four inches thick. The waste is allowed to dry and is disced six inches into the soil. For several months following, discing is repeated on a monthly basis. Although these procedures do promote degradation, the present waste application rates do not permit the maximum potential to be achieved.

As noted earlier, crops are not grown on this site; in fact, hardly any vegetation appears on the site at all due to frequent discing. Soil amendments, commonly added to agricultural soils to promote crop growth, also promote biological degradation. This site, which does not receive soil amendments, may provide for active degradation processes due to application of a nitrogen-based waste (not the API separator sludge).

Samples of wastes treated at this site are monitored on an infrequent basis for oil, water, and percent solids. The soil is monitored monthly for percent oil, percent water and percent heavy metals. Reportedly, attempts to monitor leachate migration from the site have been made, although the

TABLE 2. OPERATIONAL MANAGEMENT

	Plans/Decides Manages/Supervises	Performs	Approves Checks
Storage	E.O.		
Pretreatment	None		
Wastes Mixing	None		
Transport	E.O.	C.H.	
Application	E.O.	S.O.	
Soil Incorporation	S.O.	S.O.	
Soil Waste-Amendments	None		
Farming	None		
Monitoring	E.O.	An. Lab.	

C.H. = Contract Hauler
E.O. = Environmental Operations Staff of W.G.
S.O. = Site Operator (W.G. Employee)
An. Lab = W.G.'s Analytical Lab.

results are not considered valid by site personnel because of the methods used. While this is a fairly comprehensive monitoring strategy, the results of monitoring do not appear to be the basis for operational procedures (i.e., application rate) at the site.

SECTION 2

CONCLUSIONS AND RECOMMENDATIONS

In sharp contrast to other land disposal options, land treatment can be managed so that the waste application area need not be irreversibly removed from any other potential practical usage. The basic reason is that plant-soil systems have a natural assimilative capacity for waste constituents. If rates and total quantities of wastes applied are controlled so that the assimilation capacity of the site is not exceeded for any constituent of the waste, no potential future use of the site will be precluded. Assimilative capacity is both chemical specific and site specific. In other words, each chemical constituent of a given waste will be assimilated to a different extent at the same site; and the chemical constituents will be assimilated differently at different sites.

The conclusions of the present study are limited to the environmental acceptability of land treatment for API separation bottoms from one particular petroleum refinery at one particular application site. The results cannot be generalized, either to API separation bottoms from other plants in the petroleum refining industry, or to other potential land treatment sites for the particular API separation bottoms investigated. The field study findings do provide insight into the factors that should be considered in the design and operation of a land treatment site to ensure environmental acceptability. The field study results characterize, to the extent possible, actual practices at a land treatment site used for purposes of waste treatment rather than for purposes of research. Conditions of waste application were therefore given, and not under the control of the investigators.

CONCLUSIONS

The waste sludge as applied contained about 34% solids, 11% oil and 55% water. Approximately 1,500,000 gallons/year of waste had been applied over a 7 acre area every year for more than 10 years prior to field sampling.

Analysis of the dried waste solids showed 2% metals, 46% TOC, less than 1% TKN, SO_4 and Cl, and 51% undetermined. Of the metals analyzed,* sodium, nichel, lead, selenium, vanadium and zinc were all found at significantly higher concentrations in the application area than in the control area. The observed accumulations of the heavy metals in the upper six inches of soil are compared with the assimilative capacity of a site with a higher CEC in the table below:

---

*As, B, Ca, Cd, Cr, Cu, K, Mg, Mo, Na, Ni, P, Pb, Se, V, Zn

Metal	Observed Accumulation (kg/ha)	Assimilative Capacity CEC 15 (kg/ha)
As	10	500
Cd	3	20
Cr	2050	2000
Cu	400	500
Mo	30	
Ni	100	200
Pb	5250	2000
Se	2.5	9
V	120	500
Zn	1200	1000

The assimilative capacity is seen to have been exceeded for Cr, Pb and Zn.

Electrical conductivity, sulfate, and chloride were significantly elevated in the application area compared to the control area. Furthermore, sodium was found at higher concentrations at 6-12" depths than at 0-6" depths in the application area. These results suggest leaching of soluble sodium salts.

Total organic carbon and extractable organics were considerably higher in the application area than in the control area. Application area samples were somewhat richer in plan organics (particularly C, H, O compounds) than the waste applied indicating some oxidation degradation. However, about 80% of the extractable organics were aliphatic and aromatic hydrocarbons that apparently had persisted. Aromatics appear to be accumulating preferentially.

This site is well chosen in that the potential for groundwater and surface water to come in contact with the waste is low, and the potential of downward waste migration is impared by the high soil attenuation capacity and low permeability offered by the 14' clay layer below the site. As a result of this attenuation of the surface soils at the land treatment site exhibit elevated metal and aromatic and aliphatic hydrocarbon concentrations to a 12" depth. Although the waste/soil mixture is monitored monthly for oil, water and metals, the data generated is not used to optimize waste degradation rates or to insure the ecological integrity of the soil. However, given the nature of the site's origin, its location in an industrial complex, and its distance from residential areas, future use of the site for agricultural or residential activity is unlikely.

In summary, this site is an example of a land treatment site operated for disposal. The site itself is of poor quality (i.e., the potential for uses other than as a waste dump is minimal), although the geophysical features of the site are well suited to receive and retain waste constituents. The land treatment site management appeared to make an effort toward proper operation of the site, evidence of which is monthly discing and frequent monitoring. However, at the present rate of waste application, optimal rates of organic degradation cannot be realized due to the high loadings.

RECOMMENDATIONS

Although the site is acceptable for the present land treatment operations it will probably not be acceptable for alternative uses in the future because of pollutant accumulations at the site. A study should be performed to develop a post closure plan for this site.

SECTION 3

APPROACH

DATA COLLECTION AND ANALYSIS

Samples of the waste, baseline soil, and soil/waste mixtures were collected and analyzed for inorganic constituents and organic compound classes. Plants were collected and analysed to assess the extent of uptake of inorganic waste constituents.

The analytical protocol involved determining the following classical and inorganic waste parameters: pH, SO_4, and Cl^-, electrical conductivity (EC), cation exchange capacity (CEC), total organic carbon (TOC), total Kjeldahl nitrogen (TKN), As, B, Ca, Cd, Cr, Cu, K, Mg, Mo, Na, Ni, P, Pb, Se, V and Zn. Plasma emission spectroscopy and ion/chromatography were employed for inorganic species.

Analytical techniques employed for organic species included liquid chromatographic separation of organics into aliphatic, aromatic, and polar classes (LC-H, LC-A and LC-X, respectively), total chromatographic organics (TCO) and gravimetric (GRAV) analysis for volatile and non-volatile portions, and high resolution mass spectrometry (HRMS) for sorting classes by hydrogen saturation and heteroatom composition. The sampling and analytical methods are described in detail in the Appendix.

DATA INTERPRETATION

The analytical results from sampling the waste, the site receiving the waste, and a control site were compared to assess, insofar as possible, the relative decomposition, accumulation and migration of inorganic constituents and organic compound classes. The sampling and analytical program used in this study was designed to include sampling and analysis of appropriate control areas at the site so that any apparent concentration changes of waste components in application area samples could be differentiated from background levels. However, during preliminary site visits several factors were identified which would make it difficult to interpret any observed, apparent concentration changes. These factors include the following: an ideal control area was not available at the site; and, the chemical compositions of applied wastes were known to have varied over time.

The existence of many significant sources of uncertainty in the background data on the site made it desirable to provide some additional checks on the validity of the analytical data besides that provided by comparison of

TABLE 3. COMPARISON OF "TYPICAL" ELEMENTAL CONCENTRATION RANGES IN SOILS AND PLANTS WITH CORRESPONDING CONCENTRATION RANGES IN CONTROL AREAS USED IN THIS STUDY

Element	Typical Mean ppm Dry Soil (Range)[1]	Range ppm Dry Soil This Study[2]	Typical Range ppm Dry Plant Wt. Basis	Range ppm in Plant Ash This Study[5]
As	6 (0.1-40)	0.8-16	0.1-5[3]	1-16
B	10 (2-100)	2.1-9.2	5-30[3]	31-620
C	20,000	6,000-29,200	--	--
Ca	13,700 (7,000-50,000)	2,200-13,00	1,000-20,000	23,000-171,000
Cd	0.06 (0.01-0.7)	.3-.7	0.2-0.8[3]	1-4
Cr	100 (5-3,000)	7.9-65	0.2-1[3]	19-140
Cu	20 (2-100)	11-41	4-15[3]	69-290
K	14,000 (400-30,000)	2,300-8,400	20,400[4]	26,000-54,000
Mg	5,000 (600-6,000)	4,000-6,000	500-15,000[4]	14,000-40,000
Mo	2 (0.2-5)	1.7-3.3	0.2-5[3]	14-64
N	1,000 (200-2,500)	464-1,700	--	--
Na	6,300 (750-7,500)	22-440	--	940-10,000
Ni	40 (10-1,000)	9.6-31	10-10,000[4]	7-36
P	650	5,300-10,000	1,000-10,000[4]	17,000-168,000
Pb	10 (2-200)	24-280	0.1-10[3]	29-370
Se	7 (10-25)	0.1-0.5	0.1-2.0[3]	<.1-0.5
V	100 (20-500)	17-50	20-500[3]	3-90
Zn	50 (10-300)	41-110	10-300[3]	270-3,800

1. Bowen, H.G.M., Trace Elements in Biochemistry, Academic Press, Inc., NY, 1966.
2. CTL 0-6" Samples.
3. Allaway, W.H., Agronomic Controls Over the Environmental Cycling of Elements.
4. Berger, K.C., Sun Soil and Survival, University of Oklahoma Press, OK, 1976.
5. CTL Samples.

control and application area sample results. These checks are described below:

Inorganic Analysis

Validation of Control Samples --

The analytical data obtained in this study for control area samples from six landfarm sites are compared in Table 3 to typical concentration ranges found in soils and plants. Comparison of the soils data for the six sites indicates that almost all of the results obtained in this study are within typical concentration ranges. Exceptions are phosphorus (P), which was generally found in concentrations in excess of typical ranges, and sodium (Na) and selenium (Se), which were generally found in concentrations less than typical ranges. The selenium discrepancy may be due to volatilization of that element during the sample preparation procedure used in this study; the reasons for the sodium and phosphorus differences are not clear. Comparison of data on plants is of limited utility for several reasons, viz.: 1) plant uptake is species-specific; 2) uptake by a particular species is dependent on soil conditions; and 3) for the purpose of this study, elemental concentrations in plants have been expressed on an ash weight basis to compensate for the frequently poor physical condition of plants collected in the field. However, if we assume that the ash weight is usually on the order of 10% of the dry weight (the actual mean ash weight for all six control area samples in this study was 8.7% of dry weight), then the majority of results obtained in this study lie within typical ranges encountered in plants on a dry weight basis. In general, comparison of the results for control area samples in this study to typical elemental concentrations ranges in soils and plants suggests that there are no severe biases which would invalidate conclusions from the analytical data presented in this report.

Total Mass of Analyzed Parameters --

The sum of the masses of individual analyzed species in a sample of waste is a fraction of the total waste mass. For instance, if there were no species in the waste solids other than those determined in this study, the sum of all the individual masses should be approximately equal to 100%, depending on the uncertainty associated with the sampling and analytical methods. Inspection of the data presented shows that species determined in this study account for 68% of waste weight. The significance of this observation depends, of course, on the identity of the species that were not determined. Likely candidates are the elements Fe, H, O, Si and Al, all of which could be reasonably expected to occur in significant quantities in wastes of the type included in this study. In any case, consideration should be given to the presence of possibly substantial amounts of unidentified species in subsequent interpretations of the analytical data presented in this report.

Definition of Significant Pollutant Increases --

Interpretation requires some judgment about what constitutes a significant change in concentration of a given parameter relative to background levels. To this end, the results for total metals, Total Organic Carbon (TOC), and Total Kjelkahl Nitrogen (TKN), were expressed as ratios of total concentration in the application area to total concentration in the control area (APN/CTL).

Inspection of the data generated from six landtreatment sites indicates that three elements - K, Mg, and P - show no significant increases above background, i.e., individual APN/CTL ratios for each of the elements at each site are close to 1.0 indicating that there is little difference in the actual concentrations of each of the elements between the APN and CTL area samples. The relative standard deviations of the mean APN/CTL ratios for these three elements are 33% (K), 9.1% (Mg), and 20% (P). Their mean relative standard deviation is approximately 20%; this number may provide a useful measure of the background variability of elemental concentrations in soils. Thus, for the purpose of this report, it has been assumed that a significant change relative to background levels is indicated by a difference in the mean APN area concentration of more than $\pm$20% relative to the mean CTL area concentration (i.e., APN/CTL > 1.2).

The results for total metals, TOC and TKN in the wastes from all sites were used along with data obtained from the site owner on waste application rate (i.e., kg waste/acre/yr.) and waste percent solids, to estimate the number of years before one could expect to observe any increase of the elements analyzed in this study. The following assumptions were made:

1. Actual application rates have been the same as those given by the site operator;

2. All the waste generated for land treatment has been applied to the area which we sampled;

3. The waste has been incorporated uniformly into the top 12" of soil over the entire area described in #2; and

4. The waste composition has been constant and identical to that determined in this study.

The resulting estimates are discussed in more detail in chapter 4.

The steps in the procedure used to calculate the years of waste application necessary before one could expect to observe any increase above background were as follows.

Waste Application Rate --

The quantity kilograms of waste solids/acre/year was calculated from data supplied by the waste generator. For certain sites, the waste generator was able to provide an estimate of this quantity directly for other sites, where perhaps only an estimate of the annual volumetric waste generation rate was available, this calculation was performed according to the following equation:

$$\text{Kilograms of waste solids/acre/year} = \frac{\text{Annual volumetric mean generation} \times \text{Density of waste as applied} \times \text{\% solids in waste}}{\text{Acres of application area}}$$

In those cases where estimates of the waste density and % solids were not available from the waste generator, values obtained from laboratory analysis of waste samples collected during sampling visits to each site were used. As indicated in assumption 2 above, the value of the quantity "acres of application area" in the above equation was equal to the area in acres of the waste application area sampled in this study.

Annual Leading Rate of Individual Waste Species --

The quantity "kilograms of waste solids/acre/year" calculated in Step 1 was multiplied by the concentration in ppm of the element of interest determined in this study in waste samples collected from each site to give the annual loading of that element:

kg/acre/year x mg/kg (=ppm) of element of interest in waste solids = mg/acre/year

According to assumption 3, the waste was assumed to be incorporated uniformly into the top 12 inches of soil over the entire application area so the units of this quantity were assumed to be equal to mg/acre-foot/yr.

Annual Increase of Individual Waste Species --

The annual loading expressed as mg/acre/yr of each element of interest obtained in Step 2 was divided by an estimate of the average mass of one acre-foot of soil to give the predicted annual increase in concentration of each element of interest.*

Estimated Years of Waste Application --

The predicted annual increase in concentration of each element of interest was used to estimate the years of waste application necessary before one could expect to observe any increase above background of the elements analyzed in this study. The latter quantity depends on the detection limits of the sampling and analytical methods used for each element of interest. For example, the atomic absorption spectroscopic procedures used for analysis of many of the elements determined in this study involved digestion of ~1.5 g of soil and dilution of the resulting solution to 50 milliliters. Assuming that our instrumental method was capable of detecting a change in concentration

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[The average mass of one acre-foot of soil was calculated as follows:

1 acre ~ 43,560 ft^3; 1 acre-foot =
43,560 ft^3 x 1 ft = 43,560 ft^3;
43,560 ft^3 x .0283 m^3/ft^3 = 1233 m^3;
average bulk density = 1.6 g/cm^3 = 1.6 x 10^3 kg/m^3 (cf. Overcash, M.R. and D. Pal, Design of Land Treatment Systems for Industrial Wastes Theory and Practice, Ann Arbor Science, 1979);
1233 m^3 (1.6 x 10^3 kg/m^3) $\simeq$ 2 x 10^3 kg
Therefore,
(mg/acre-foot/yr) $\simeq$ 2 x 10^6 kg/acre-foot = $\frac{\text{mg of element of interest}}{\text{kg of soil-year}}$ =

ppm/year]

of the element of interest in that solution equal to 1 part per million, the corresponding concentration change of that element in the soil sample taken for analysis would be $\sim$ 30 parts per million:

$$\left(\frac{1\mu g}{mL} \times 50\ mL\right) / 1.5\ g \simeq 30\mu g/g = 30\ ppm\ in\ soil$$

The quantity ppm/year calculated in Step 3 was divided by 30 ppm to give the number of years of waste application necessary to observe a concentration change. Note that the "observable concentration changes" referred to here are not the same as "significant concentration increases" referred to in the preceding discussion.

For most elements determined in this study by atomic absorption (AA), the actual instrumental detection limit is probably lower than 1 ppm. However, since a systematic study of the detection limits of the combined sampling and analytical methods was beyond the scope of this study, the 1 ppm estimate may, in fact, be a more reliable estimate of the actual detection limits, given the uncertainty associated with the sampling methods.

Organic Data Interpretation

The principal objective of the organic chemical analysis program was to obtain data for a preliminary evaluation of the effectiveness of land treatment in degrading organic components of chemical wastes. To accomplish this objective it was necessary to characterize the organic components of the waste and to look for evidence of significant accumulation, degradation or migration of those components in the soil.

The organic analysis scheme provided for quantitative analysis of extractable volatile (TCO) and non-volatile (GRAV) organics, and of three polarity classes (LC-H, LC-A and LC-X) by liquid chromatography. Qualitative analysis of the organics by compound type was achieved by HRMS which provided data on heteroatom composition and the degree of compound saturation (R + DB values).

The combined qualitative and quantitative results provide insight into the extent of waste component degradation. For instance, an increase in polar species in APN area samples can be taken as an indication that the aromatic and aliphatic constituents originally in the waste have partially degraded since the byproducts of aerobic oxidation are generally polar oxygenated species. Typically, the organic analysis results do not permit determination of which waste components are being transformed into particular types of degradation products. However, the HRMS data do indicate which specific classes tend to persit in the soil column and which classes tend to appear as degradation products.

Accumulation of certain waste types can be determined by increases of aromatic and aliphatic classes relative to each other. For example, suppose the LC-H and LC-A fractions of extractable organics account for more than 50% of the organics in the APN 0-6 and 6-12 layers and in the control soil in

these fractions are only 10% of the total. The ratio of LC-A to LC-H in the waste is 0.24; in APN 0-6, 0.37 and in APN 6-12, 0.96. The absolute values of the LC-H and LC-A concentrations were lower in the APN 6-12 than in the 0-6. These types of trends are indicative of 1) preferentially degradation/or loss of aliphatic waste constituents over that of aromatic hydrocarbons, and 2) of aliphatic waste constituents over that of aromatic hydrocarbons, and 2) in the APN soil compared to the CTL soil, without the appearance of oxidative degradation.

SECTION 4

RESULTS AND DISCUSSION

WASTE CHARACTERISTICS

Total Mass of Parameters Analyzed

Approximately 49% of the dried solids have been identified, of which 95% are organic carbon. The remaining solids may include the elements Fe, H, O, Si and/or Al. The solids identified were analyzed as follows:

	%
Metals	2.07
TOC	46.46
TKN	0.23
SO_4	0.14
Cl	0.0023
	48.9

Inorganic Analysis

The results of analysis for total metals, TOC and TKN in the waste are presented in Table 4. These data were used along with data on waste application rate (2.4×10^7 kg/yr over 7 acres), and % solids (34%) to calculate an estimate of the years of waste application necessary before one could expect to observe any increase above background in the application area soils. Section 3 details the assumptions used in estimating this quantity. Based on the calculation, observable increases of elements in soils at the time of sampling would be expected for all elements except B and Cd.

Organic Analysis

The waste was found to contain 77 g/L of extractable organics. On the basis of the LC separation of the extract, the organic materials could be characterized as follows:

Aliphatic Hydrocarbons,	volatile (TCO):	20% (15.4 mg/L)
	non-volatile (GRAV):	31% (23.9 mg/L)
Aromatic Hydrocarbons,	volatile (TCO):	11% (8.5 mg/L)
	non-volatile (GRAV):	27% (20.8 mg/L)
Polar Organics,	volatile (TCO):	8% (6.2 mg/L)
	non-volatile (GRAV):	4% (3.1 mg/L)

TABLE 4. INORGANIC WASTE ANALYSIS AND ESTIMATED YEARS BEFORE OBSERVABLE SOIL CONCENTRATION INCREASES

Element	Waste Concentration (ug/g dried solids)	Estimated Years of Waste Application for Observable Soil Concentration Change
As	8	1
B	4	*
TOC	46.5%	1
Ca	8600	1
Cd	2	*
Cr	1600	1
Cu	160	1
K	1900	1
Mg	3400	1
Mo	10	5-10
TKN	0.23%	1
Na	3000	1
Ni	44	2
P	750	1
Pb	93	1
Se	3	1
V	26	3
Zn	1100	L

* = greater than 10 years

The recovery from the LC column for this sample was 87%. The data above have been normalized to 100%. The presence of almost 40% by weight of TCO range organics is significant in that those materials are likely to undergo evaporative transport from soil to air, in addition to possible degradation in the soil.

The results of the HRMS analysis of the waste extract are presented in the R+DB summary matrix (Table 5). The range of hydrocarbons and very low levels of polar species tend to confirm the petroleum origin of this waste. The waste was found to contain a wide variety of unsaturated and aromatic hydrocarbons including polynuclear aromatics with three (R+DB 10) to five (R+DB 15) fused rings. No, C, H, N compositions were identified, and only very small quantities of C, H, O material were found. The ELCOMP data indicated only single oxygen atom compositions. Sulfur-containing species, primarily aromatic (R+DB 5-12) were the most abundant polar materials found. The majority of the C, H, S compositions identified by ELCOMP corresponded to relatively high molecular weight (200-300) material. It is rather uncommon to find appreciable amounts of R+DB 9, C, H, S material in an organic waste without also finding the C, H, O and C, H, N analogs; however, that is the situation found for the site waste.

SOIL CHARACTERISTICS

No appropriate control area was available in the vicinity of this site. The area chosen for control was the backside of the western berm surrounding the application area. The "control" samples analyzed apparently reflect the long-term use of this area for waste disposal, and/or the source of soils sued for berm construction. The site was sampled on November 9, 1979.

Inorganic Analysis

Inorganic analytical data on soils is presented in Table 6. To assess significant changes with respect to background, the results for total metals, Total Organic Carbon (TOC), and Total Kjeldahl Nitrogen (TKN), have been expressed in ratios of total concentration in application area to total concentration in control area. These "APN/CTL ratios" are also shown in Table 6. As discussed in Section 3, for the purpose of this report, it was judged that a significant change relative to background levels is indicated by a difference in the mean APN area concentration of more than 20% relative to the mean CTL area concentration (i.e., APN/CTL 1.2). For one year of waste application, the concentration increases, as discussed under "waste Characteristics" of this Section, were predicted for every element analyzed except for B and Cd. in the following order for the first seven elements:

TOC Ca Mg Na K Cr N

The observed increase of elements were in very good agreement with the predicted values, although the concentration ranking was slightly different than predicted, as shown below:

TOC Ca Na Pb N Cr Zn

TABLE 5. R+DB SUMMARY MATRIX FOR SITE WASTE SAMPLE*

R+DB	C,H	C,H,O	C,H,S	Total (from HRMS Analysis)
0				0
1	12.0			.2
2	8.0	0.1		8.1
3	6.1	0.1	0.4	6.6
4	9.0		0.4	9.4
5	3.0			3.0
6	2.6		0.1	2.7
7	4.0			4.0
8	2.4		0.3	2.7
9	4.4	0.2	5.8	10.4
10	13.8		0.7	14.5
11	4.3		0.8	5.1
12	6.5	0.1	1.2	7.7
13	1.7			1.7
14	3.8			3.8
15	0.9			0.9
16	0.4			0.4
17	0.5			0.5

*All data in percent, normalized to 100%.

TABLE 6. TOTAL METALS, TOC, TKN, APN/CTL RATIOS

	Concentration in Soils (µg/g dry wt.)				
	CTL		APN		
Element	0-6"	6-12"	0-6"	6-12"	APN/CTL*
As	0.8	1	4	1	2.8
B	5	5	6	5	1.1
TOC	0.78%	NA	10.97%	NA	14.1
Ca	1.3%	1.9%	1.8%	2.0%	1.2
Cd	0.3	0.7	1.3	1.3	2.6
Cr	65	70	820	1000	13.5
Cu	27	25	160	150	6.0
K	3100	3200	3300	3000	1.0
Mg	4500	5700	6000	4800	1.1
Mo	3.3	4.3	12	12	3.2
TKN	464	NA	0.22%	NA	4.7
Na	410	680	1400	2900	2.9
Ni	19	23	41	39	1.9
P	5300	7300	4400	6800	0.9
Pb	280	120	2100	1100	8.0
Se	0.1	0.1	1	0.5	7.5
V	17	23	48	65	2.8
Zn	67	52	480	550	8.7

* APN/CTL Ratio = $\frac{PPM_{APN\ 0\text{-}6" + APN\ 6\text{-}12"}}{PPM_{CTL\ 0\text{-}6" + CTL\ 6\text{-}12"}}$

NA = Not Analyzed

This good agreement was not expected because the site had received waste for greater than a one-year period. Possibly, the control area soils at this site were contaminated with waste, thereby decreasing the level of observable increases.

Conclusions concerning downward migration of the inorganic constituents cannot be drawn from these results because of the heavy application rates and the significant amount of waste material observable in the core samples from both depths.

Data for pH, CEC, sulfate, chloride and electrical conductivity are given in Table 7. The increased electrical conductivity, $SO_4^{=}$, and Cl^- levels in the APN area samples suggest that cations (e.g., Na) which appear to increase in concentration in the APN 6-12" sample relative to the APN 0-6" sample may exist as soluble salts. While salinity and elevated sodium levels are of concern at agricultural sites, the only potential hazard posed at this site would be surface runoff carrying the salts into the wastewater lagoon.

Organic Analysis

Control Area

Ten control samples - one composite from 0-6" depth (CTL 0-6) and one composite from 6-12" depth (CTL 6-12) in the control plots at each of five sites studied - were analyzed, to characterize the extractable organic materials that might be found in a range of natural soils. Because of difficulties encountered in establishing control areas in this program, this characterization of control soils is an especially important reference point.

Table 8 presents data on the total organic carbon content and the quantity of extractable organic material in each control sample. It is obvious that a small and highly variable portion of the soil organic material is extracted by methylene chloride. Known types of non-extractable organics include high molecular weight polymeric materials, such as amino acids. Non-polar and moderately polar organic species of molecular weights up to 500 or 1000 are generally efficiently extracted from environmental samples by methylene chloride. All of the extracted material is in the GRAV range (b.p. >300°C) which is expected, since TCO range organics (b.p. 100-300°C) would be lost from soil by volatilization. Also expected is the observation that CTL 6"-12" samples have considerably lower levels of extractable organics than CTL 0"-6" samples. However, the levels of extractable organic material from this site especially CTL 0-6" samples exceed the range of extractable material from the other four sites studied by at least an order or magnitude. This is one of several consistent indicators that the site control had a past history of contamination.

The results of the LC separation and HRMS analysis for the site control sample extracts are presented schematically in Figures 1 through 4. The results of LC separation, for both the CTL 0-6" and CTL 6-12" samples, show a pattern in which aliphatic hydrocarbons constitute the largest fraction. The HRMS analysis for the CTL 0-6 sample (Figure 3) displays a pattern in

TABLE 7. INORGANIC PARAMETERS

Sample	pH	C.E.C. meq/100g	E.C. umhos	$SO_4^=$ µg/g	Cl µg/g
Waste				1400	23
Soil:					
CTL 0-6	7.8	31.7	670	200	13
CTL 6-12	8.0	22.9	760	300	11
APN 0-6	7.5	22.2	8400	4300	150
APN 6-12	7.5	30.9	4900	1.9%	60

TABLE 8. QUANTITIES OF TOTAL AND EXTRACTABLE ORGANIC MATERIAL IN CONTROL SOIL SAMPLES

	Organic Material, mg/kg	
	Total Organic Carbon	Extractable Organic
CTL 0-6"	7,800	2,440
CTL 6-12"		550

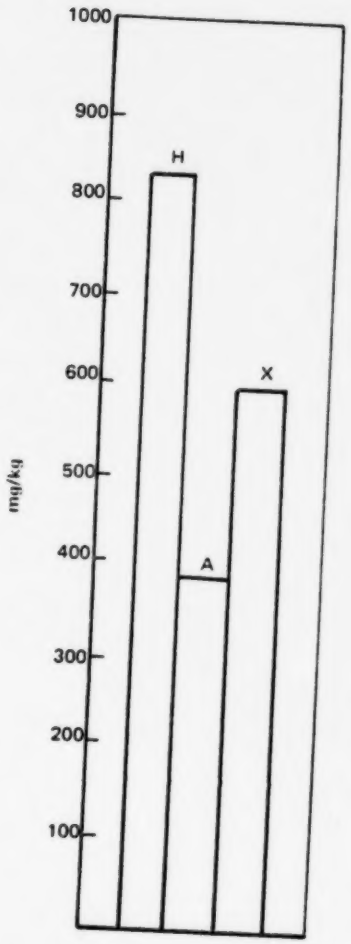

FIGURE 1 LC RESULTS FOR CTL 0-6 SAMPLES

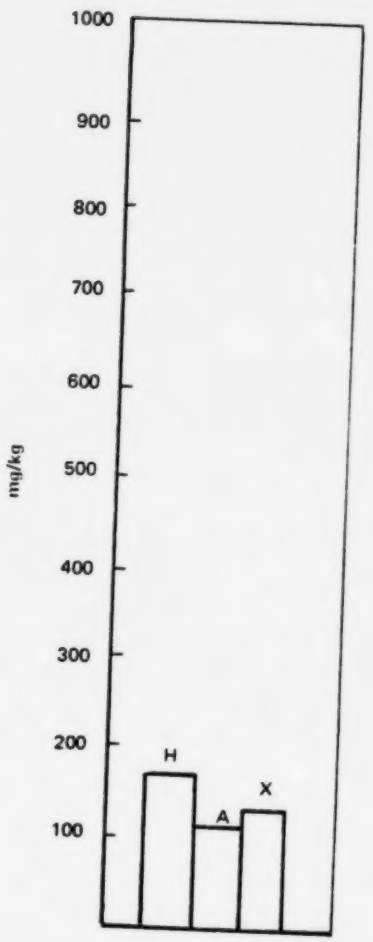

FIGURE 2 LC RESULTS FOR CTL 6-12 SAMPLES

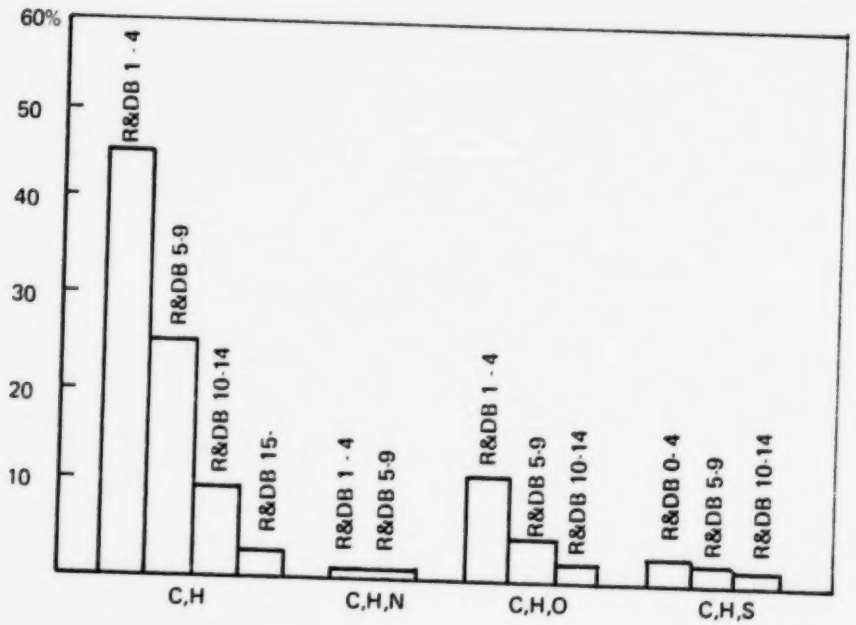

FIGURE 3 SCHEMATIC R+DB CLUSTER SUMMARY FOR CTL 0-6 SAMPLES

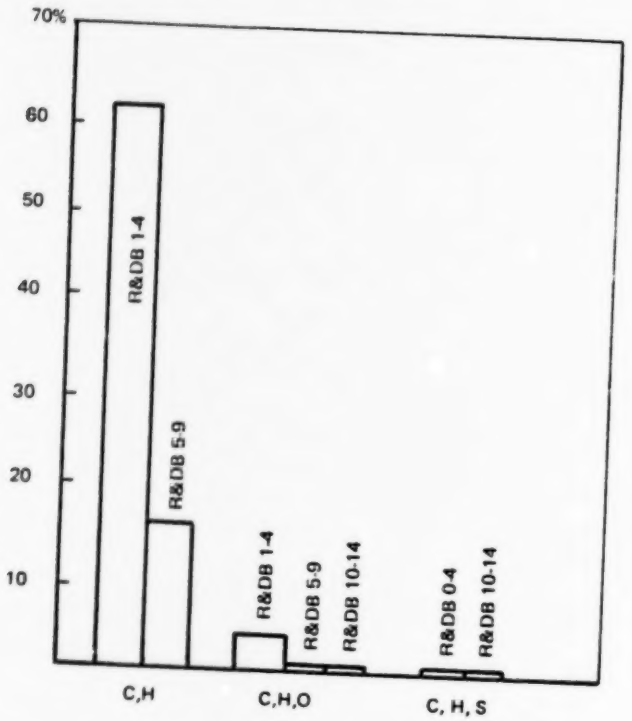

FIGURE 4 **SCHEMATIC R+DB CLUSTER SUMMARY FOR CTL 6-12 SAMPLE**

which a large portion of hydrocarbons are in the ring plus double bond (R+DB) classes 5-9. Control plot samples from other sites were characterized by predominantly polar organics. This presents further evidence that waste-type constituents are present in the control soils at this site, a situation that must be kept in mind in analysis of waste application soils.

Application of Area Soils

The application area 0-6" depth (APN 0-6) and 6-12" depth (APN 6-12) samples were found to contain 90 g/kg and 99 g/kg, respectively, of extractable organic material. These values are substantially higher than the corresponding levels for the "control" samples at the site: 2.44 g/kg for CTL-06 and 0.55 g/kg for CTL 6-12. These data imply that there has been a significant accumulation of extractable organic material in the application area soil samples, over and above the high levels observed for the control samples.

Figure 5 presents the results of the LC separation of the site application area samples, as well as the corresponding waste and control area samples. The APN 0-6 and APN 6-12 fractionation patterns are very similar both qualitatively and quantitatively. These data imply that the APN area is homogeneous down to at least a 12" depth. Comparison of the APN and waste sample results reveals that the APN samples are relatively somewhat richer in polar organics (LC-X = 21% of total) than is the waste (LC-X = 12% of total). This shift in distribution is in the direction that would be expected if some oxidative degradation of waste components were occurring in the application area. On the other hand, waste aliphatic plus aromatic hydrocarbons account for about 80% of the APN sample extracts. This implies that a major portion of LC-H and LC-A material from the waste has remained in the soil without undergoing oxidative degration. This raises the questions about the toxicity and migration potential of the accumulated constituents.

Compared to the waste sample, the APN samples are considerably depleted in volatile (TCO) materials (14% of APN 0-6 versus 39% of the waste extract). Examination of the LC-H and LC-A data for the non-volatile (GRAV) materials reveals some evidence for selective degradation/accumulation of waste components. In the waste itself LC-H constitutes 50% of the GRAV range material and the LC-A to LC-H ratio is 0.87. In the APN 0-6 and 6-12 sample extracts, LC-H constitutes 38% of the GRAV range material and the LC-A to LC-H ratio is 1.1. The data imply that there is some preferential accumulation of aromatics.

In Figure 6 the R+DB cluster profiles, on a relative distribution basis, are plotted for the waste, APN 0-6, APN 6-12 and CTL 0-6 samples. Figure 7 presents similar profiles in which the R+DB data have been weighted to reflect the differences in total quantities of extractable materials in the various samples. The similarity of the APN 0-6 and 6-12 samples is confirmed by the R+DB cluster profiles and by the details of the ELCOMP listings as well.

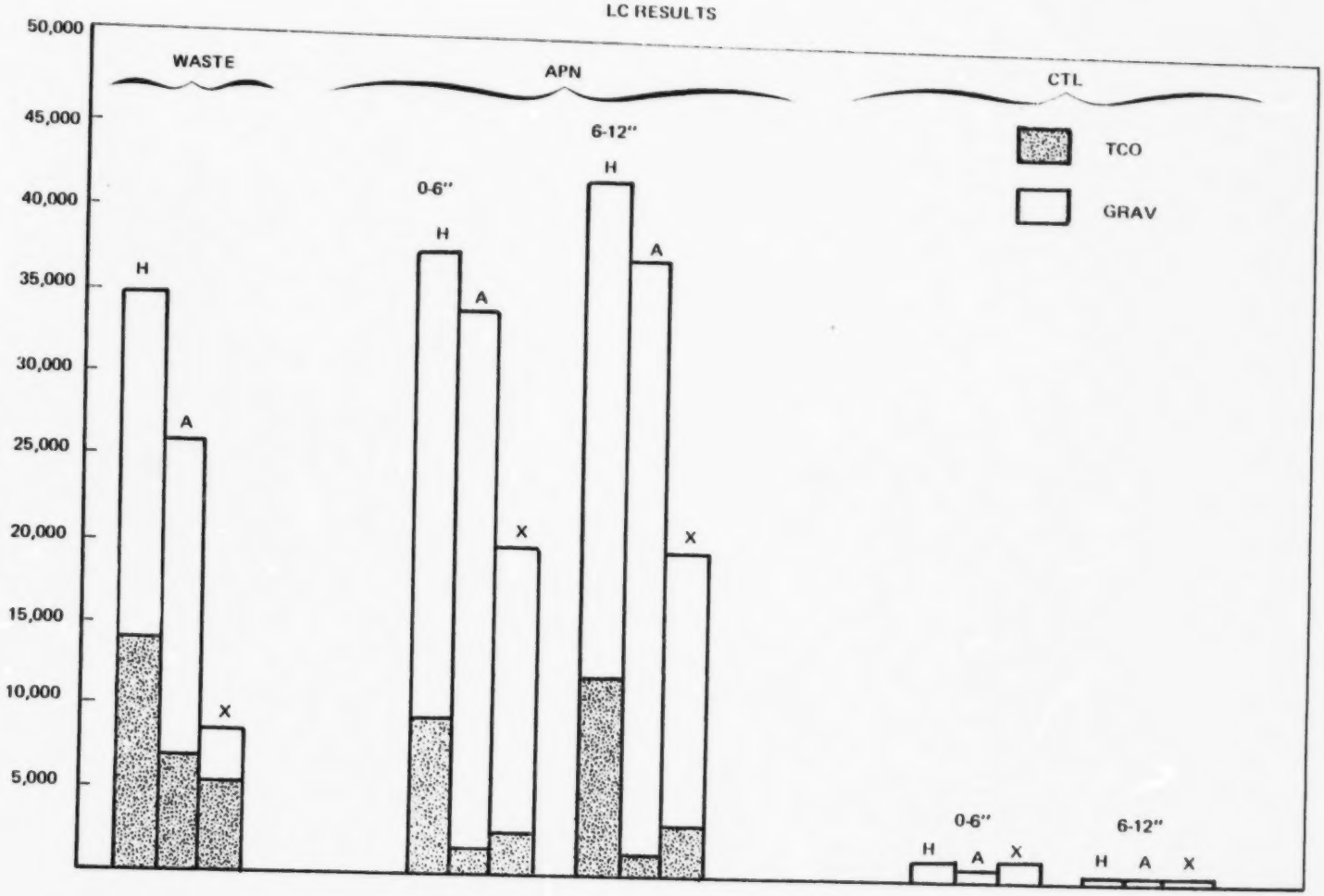

FIGURE 5 SCHEMATIC REPRESENTATION OF LC SEPARATION INTO ALIPHATIC (H), AROMATIC (A) AND POLAR (X) ORGANIC CLASSES.

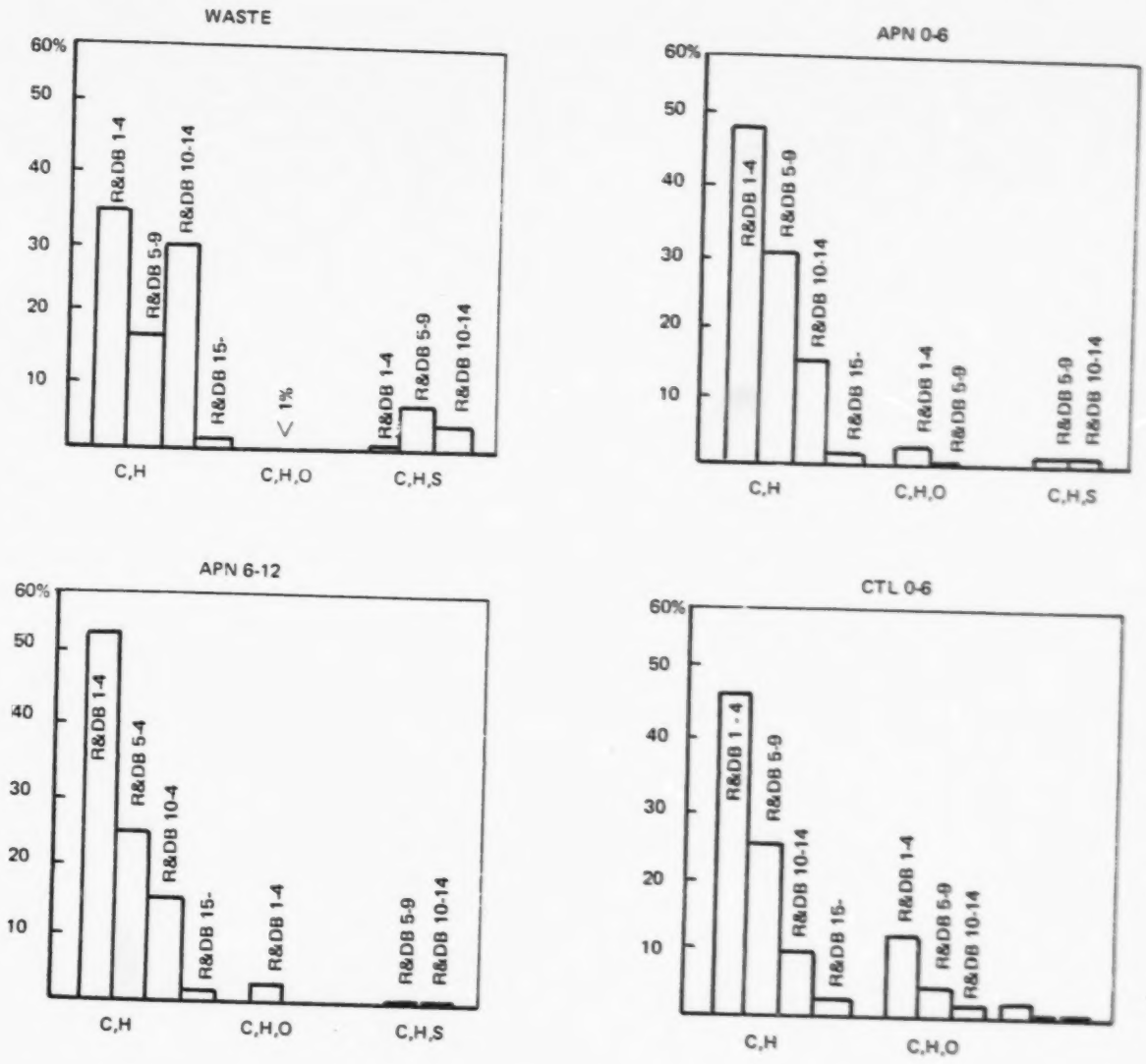

FIGURE 6 R+DB CLUSTER PROFILES, RELATIVE ABUNDANCE BASIS

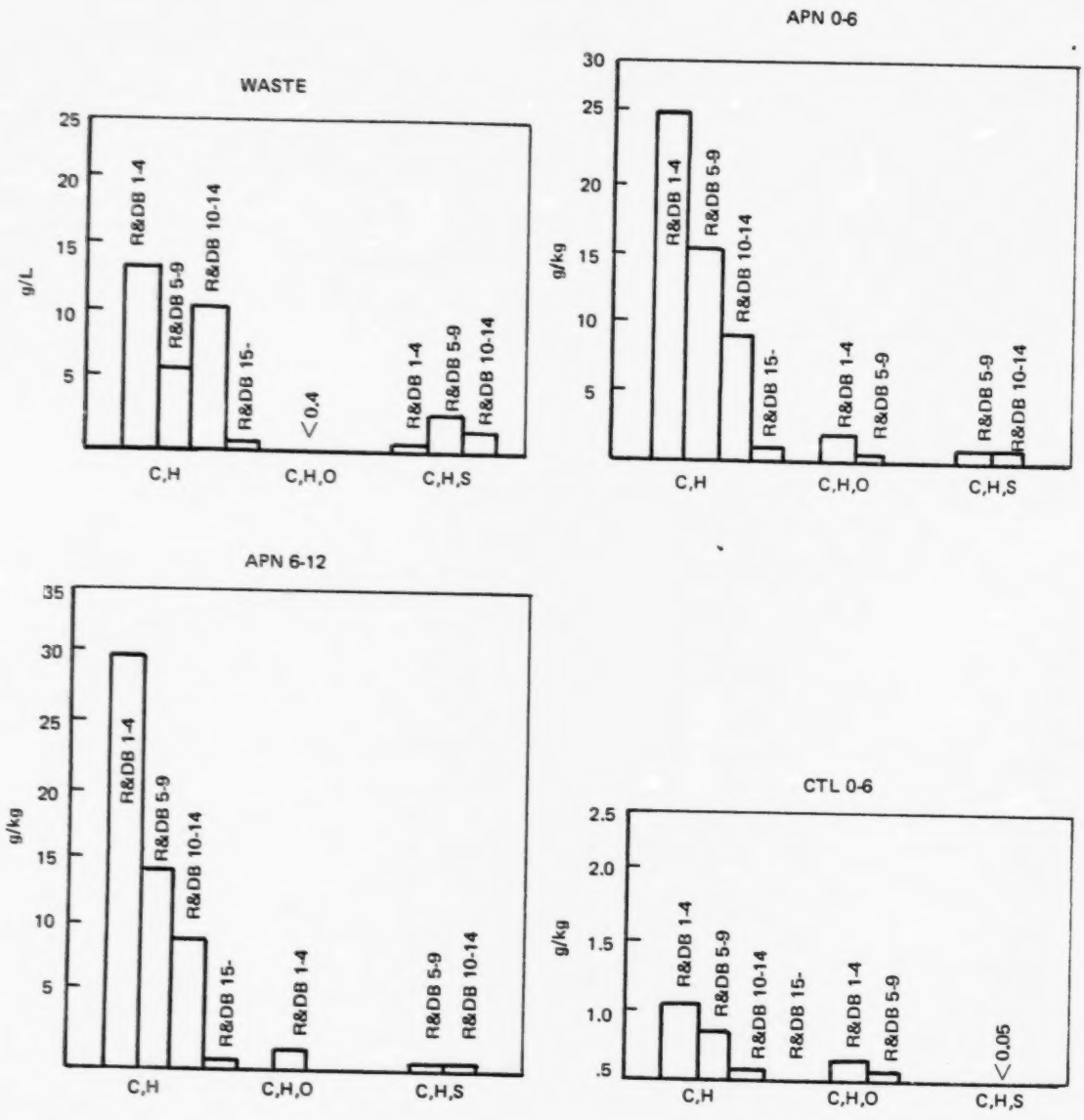

FIGURE 7 R+DB CLUSTER PROFILES, WEIGHTED BASIS

There are some potentially significant differences between the waste and the APN in the R+DB cluster profiles and in the supporting ELCOMP assignments. The APN area samples are relatively richer in R+DB 0-4 C, H species. Furthermore, the APN C, H materials are almost all low molecular weight ions (<200), while the waste R+DB 0-4 hydrocarbons range up to mw 300. The waste sample is richer in R+DB 10-14 range aromatics -- primarily an anthracene/phenanthrene series in R+DB 10 and pyrene series in R+DB 12 -- than are the APN samples. In this category, however, APN area samples merely show lesser abundances of the same range of compositions as the waste. The irregular R+DB profile observed for the waste C, H category is suggestive that this particular sample may represent a deviation from the "normal" site waste. It seems more plausible to presume that the waste was somehow spiked with abnormal quantities of R+DB 10 and 12 aromatics than to infer that those two categories of PAH's were selectively lost/ degraded in preference to higher and lower PAH's.

The C, H, O data for the APN area samples show evidence of R+DB 1-4, O_2 and O_3 species, which confirm that some oxidative decomposition of waste materials has occurred. The slight differences in the C, H, S R+DB profiles cannot be interpreted with confidence, since the same ions are generally identified by ELCOMP in all samples examined for each R+DB category. There is some tendency toward fewer, lower molecular weight C, H, S species in the APN samples than in the waste.

Based on the above results one can draw the following inferences about the accumulation and degradation of organic waste components at this land treatment site:

i. Extractable organic material has accumulated in the application area.

ii. There is evidence for slight enrichment in polar material, including oxygenates of the type that indicate that some oxidative degradation of the waste components has occurred.

iii. Considerable quantities of aromatic and aliphatic hydrocarbons have accumulated without undergoing oxidation.

iv. The volatile materials in the waste appear to have been preferentially lost, although volatiles still account for 14% of the extractable APN area materials.

v. There is some evidence for selective accumulation of aromatic compared to aliphatic hydrocarbons in the APN area.

vi. It seems plausible that the apparent levels of R+DB 10 and 12 C, H materials in the waste represent a peculiarity of the waste sample and do not imply selective loss of these species from the APN area.

PLANT ANALYSIS

No plants were growing in the application area where soil samples were collected. Thus, plant samples were collected from the edges of this

area with an attempt to gather individual plants growing closest to the oily waste application itself in order to gain some understanding of heavy metal uptake where waste application had been very heavy. With no typical agronomic species present, samples collected were largely saltgrass with some sow thistle mixed in. "Control" samples were taken from the berms surrounding the application area, but could not be considered true controls. The plant samples analyzed were two subsamples taken from two different areas within the so-called control area. Data for total metals in these samples are given in Table 9. Differences in observed plant content in the two control sample bags could be reflective of differences in where the plants were found growing. It is also possible that the two sample bags contained different proportions of saltgrass and thistle, although very little of the latter was collected. Control 2 apparently contained higher proportions of most of the elements examined. Plant/soil and control/application plant ratios were not computed as they would have little meaning for this site. DTPA extractable metals, an indication of metals available for plant uptake, are given in Table 10.

Conversion of these ash weight concentrations to a dry weight basis indicate elevations in chromium, copper and lead above ranges considered typical for agronomic species. The plants sampled were not agronomic species and caution must be exercised as some grass species are known accumulators of heavy metals. Important here, however, is the fact that these "control" plants, growing on fill constructed of dredge spoil and adjacent to an area of very heavy refinery waste application, do not represent a baseline, or control for plant uptake of waste constituents.

TABLE 9. PLANT SAMPLE CONTENT OF TOTAL ELEMENTS AS ANALYZED IN ASHED SAMPLES

Element	Concentration (µg/g) ash	
	CTL 1	CTL 2
Ash	6.7%	9.0%
As	2	5
B	60	82
Ca	7.7%	7.6%
Cd	2	2
Cr	140	220
Cu	180	220
K	2.6%	3.5%
Mg	2.6%	2.5%
Mo	44	78
Na	1.0%	7400
Ni	31	36
P	1.4%	1.6%
Pb	370	411
Se	0.3	0.7
V	46	48
Zn	1100	900

TABLE 10. SOIL SAMPLES: DTPA EXTRACTABLE METALS

	Concentration (µg/g)			
	CTL		APN	
Element	0-6"	6-12"	0-6"	6-12"
As	NA	NA	NA	NA
B	0.3	0.3	0.6	0.7
Ca	NA	NA	NA	NA
Cd	<.1	<.1	0.1	0.2
Cr	0.1	0.1	0.4	0.1
Cu	4	3	0.1	56
K	72	47	72	500
Mg	264	272	490	0.1
Mo	<.1	<.1	0.4	650
Na	100	234	1700	5
Ni	3	3	5	21
P	48	40	43	NA
Pb	NA	NA	NA	NA
Se	NA	NA	NA	0.1
V	0.6	0.5	0.3	65
Zn	6	3	37	

APPENDIX

METHODS OF SAMPLING AND ANALYSIS

DATA COLLECTION PROCEDURES

Several approaches were used to collect data from the six field sites selected for study. Information sources included published surveys such as those produced by the Soil Conservation Service and/or local universities and state agencies. Where feasible, information gathered from interviews with site or industry personnel along with site observations were utilized to confirm or adjust such information for location specificity.

FIELD SAMPLING

The field sampling and analysis program was designed to provide information on the following:

1. The rate and extent of waste degradation,
2. The migration of inorganic species,
3. The accumulation of waste constituents in the soil, and
4. Bioaccumulation of inorganic species in vegetation.

To this end, measurements were made of the concentration of various chemical species in soil and vegetation samples taken from waste application and control areas. The species selected for analysis were those that occur as a direct result of the land cultivation operation and/or transport of any constituents of the wastes.

Sampling Methods

Sampling Locations--

At each site, samples were taken from (1) the area where waste had been applied and (2) the best identifiable control area. The ideal control area would have been upwind and upgradient of the waste application area, but in all other respects would have been identical to that area except that no waste had been applied. Selection of an appropriate control area was a problem at the majority of sites for a variety of reasons. In general, the design and operation of most sites did not include provision for a bona fide control area as described above. More specifically, problems included substantial variations in soil characteristics, drainage patterns and vegetation occurring within small distances; and uncertainty about the history of waste application outside the boundaries of the present application site. In all cases, a "control" area

was selected which necessitated the least compromise in the requirements stated above. In both control and application areas, samples were collected from a 4 x 4 grid covering the area. Wastes were collected from storage facilities or other sources, selected so as to assure that the samples were representative of the waste that was actually applied.

Sample Types--

The types and numbers of samples collected at each site included at a minimum the following:

	Control Area	Application Area
1) Waste	1 Sample	
2) Soil	2 Samples	2 Samples
3) Soil-Waste Mixture	-	2 Samples
4) Vegetation	1 Sample	1 Sample

Core samples of soil and soil-waste mixture were taken with a sampling tube. The resulting cores were 1" in diameter and 12" in length. These samples were divided in the field into two subsamples corresponding to 0-6" soil depth and 6-12" soil depth. Bulk samples were subsequently coned, quartered, and riffled to obtain amounts of sample appropriate for each analysis. Vegetation samples were collected from the same control and application areas from which soil samples were obtained. Unless noted otherwise, composite vegetation samples were prepared from whole plants minus roots. There were no opportunities for sampling surface water, runoff, or groundwater at any site during the sampling visits made.

CHEMICAL ANALYSIS

Inorganic

Analyses of inorganic parameters were conducted on the waste samples, soil and soil-waste mixture composite samples from application and control areas, and vegetation composite samples from application and control areas. Analytical methods used for determination of inorganic parameters are shown below. DTPA-Extractable metals are those metals which may be available for biological uptake.

Parameter	Method
B, Cu, Cd, Cr, Cu, K	HNO_3-$HClO_4$ digestion, plasma emission spectroscopy
Mg, Mo, Na, Ni, P, Pb, V, Zn	
As, Se	Hydride evolution, atomic absorption spectroscopy

Total Organic Carbon (TOC)	Combustion, gravimetric
Total Kjeldahl Nitrogen (TKN)	Digestion, distillation, volumetric
Sulfate	0.1 M LiCl extraction, ion chromatography
Chloride	H_2O extraction, volumetric $Hg(NO_3)_2$ titration
Cation Exchange Capacity (CEC)	Volumetric
Electrical Conductivity (EC)	Conductivity Meter
pH	pH Meter
DTPA-extractable metals	DTPA extraction, plasma emission spectroscopy

Organic

The organic analysis scheme is shown schematically in Figure 8 . The methodology involved:

1. Solvent extraction with methylene chloride;
2. Quantitative analysis of volatile and non-volatile organics;
3. Liquid chromatographic separation of the extracts to divide the organics into three polarity classes: aliphatic hydrocarbons, aromatic hydrocarbons, and polar species; and
4. Qualitative analysis of organic compound classes present by high resolution mass spectrometry.

Each of the steps of the methodology is described in further detail below.

Extraction--

The method adopted for isolation of organic components from the waste and soil samples was extraction with methylene chloride. Methylene chloride is a solvent which gives high extraction efficiency for a wide range of organic compound types. In particular, it is generally effective for non-polar and moderately polar, hydrophobic organics, which are the types of compounds that dominate many current lists of compounds of concern. It should be recognized, however, that polymeric, humic, proteinaceous materials, very polar, water-soluble, or soil-bound species will not be efficiently extracted. It should also be noted that these non-extractable species, if isolated, would generally not be amenable to available analysis techniques. An organic compound which is extractable from a waste sample may not be extractable from a corresponding soil sample because of soil bonding. Since non-extractable organics are probably less likely to be transported into plant cells, they may be of less environmental concern.

Control and application area soil samples (ca 100 g) were Soxhlet extracted with methylene chloride (ca 200 mL) for 24 hours. Waste samples were

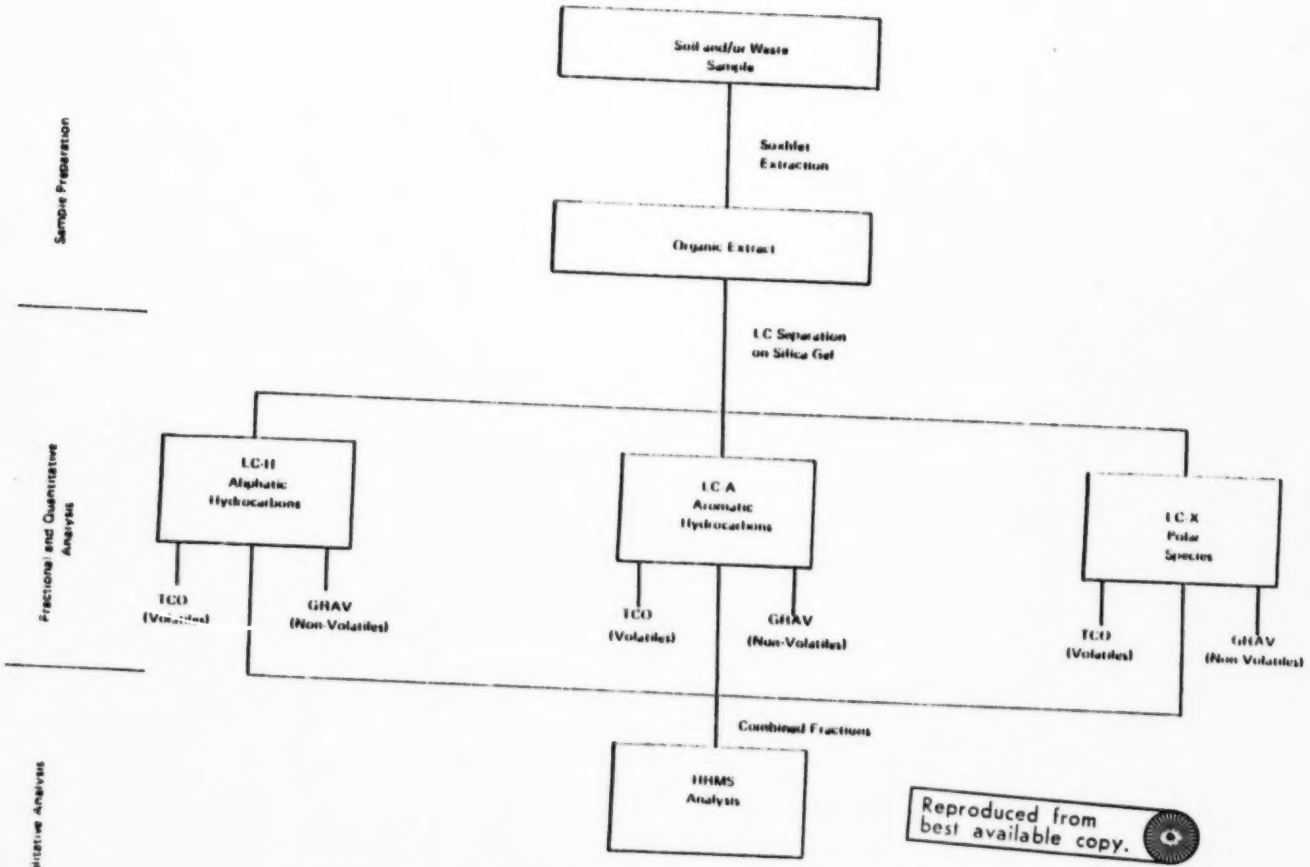

FIGURE 8. FLOW CHART OF PROPOSED ORGANIC ANALYSIS SCHEME

subjected to Soxhlet extraction, or to liquid-liquid separatory funnel extraction (3 times 100 mL of solvent per liter of waste), depending on their physical state. The methylene chloride extracts were concentrated to 10 mL final volume by use of Kuderna-Danish evaporative concentrators.

Quantitative Analysis--

Total Chromatographable Organics (TCO)--The Total Chromatographable Organics (TCO) analysis is a gas chromatographic (GC) analysis procedure that uses a flame ionization detector. A 1-5μL aliquot of the sample is injected. Resolution of individual QC peaks is not intended. The total integrated detector response is used to derive a single estimate (mg) of the quantity of material in the 100-300°C boiling point range.* The detection limit for a complex sample mixture is on the order of 50 ppm (w/v) in the solution injected. This corresponds to 0.5 mg total in the 10 mL sample extract.

Gravimetric Analysis (GRAV)--The GRAV procedure is a quantitative analysis of non-volatile components (materials above 300° boiling point range) of the sample extract. An aliquot of the organic solution is evaporated to constant weight, over silica gel, in a tared weighing dish. The practical detection limit is on the order of 0.1 mg in the 1 mL sample taken for GRAV analysis. This corresponds to 1 mg total in the 10 mL sample extract.

Liquid Chromatographic Separation--

A liquid chromatographic (LC) separation on silica gel was used to separate the extracted organics according to polarity. This is a lowresolution technique that has been demonstrated at Arthur D. Little, Inc. to provide reliable separation of organic components into three classes as indicated below.

LC-H: Aliphatic Hydrocarbons

LC-A: Aromatic Hydrocarbons

LC-X: Polar Organics (oxygenates, amines, etc.)

Details of preparation of the silica gel LC column have been published. The methylene chloride extracts were applied to the column after solvent exchange into cyclohexane. The elution sequence used in this program was as follows:

LC-H: 15 mL of pentane

LC-A: 15 mL each, sequentially, of 20% methylene chloride in pentane; 50% methylene chloride in pentane; and methylene chloride

* Arthur D. Little, Inc., studies using model compounds have shown that n-hexadecane (b.p. 303 C) defines a reasonable break point between TCO and GRAV range materials.

LC-X: 5 mL each, sequentially, of 5% methanol in methylene chloride; 20% methanol in methylene chloride, and 50% methanol in methylene chloride.

Each fraction was analyzed by TCO and TRAV procedures as described above. The fractions were then recombined prior to HRMS analysis.

The LC procedure was originally scaled for 15-100 mg samples applied on column. However, the total amount of material available for some samples in this program was 10 mg. Quantitative recovery from the column was 70-100% when samples containing about 10 mg or more were used, but 50% for very small samples.

The reproducibility of the extraction and LC separation for these samples was checked by running duplicate LC columns on a site application area soil extract. The results are shown in Table 11.

High Resolution Mass Spectrometry--

High resolution mass spectra were obtained on the recombined LC fractions for each of the landfarm sample extracts. A Dupont (CEC) 21-110 B high resolution mass spectrometer, using a glass inlet and solids probe for sample introduction, was employed. Spectra were recorded on photoplates. The basic spectral data were then obtained by a photoplate reader and the position and intensity of the lines transferred directly to a laboratory data system (LDS). This is the HIRES output. The LDS, based on a Data General Elipse S/200 computer, was used for subsequent HRMS data processing.

The high resolution mass spectrometer is capable of measuring masses of ions in the spectrum with an accuracy of better than 0.001 atomic mass unit. Data from the HRMS analysis are reported to four decimal places in m/e (mass-to-charge ratio). The high accuracy and precision makes it possible to take advantage of the mass defect characteristics of atoms and use their exact masses to compute elemental composition assignments for the observed ions. The theoretical mass can be calculated for all "plausible" combinations of elements corresponding to a given mass. "Plausible" combinations are defined by the analyst, based on a preliminary manual examination of the HIRES data. The objective is to allow all of the elemental compositions (C + H; C + H + S; C + H + Cl, etc.) that are necessary to characterize the range of the sample chemistry, but to minimize the computation time and the number of incorrect, "near-miss" match assignments. The theoretical and measured masses are next compared and a "match" is identified when they agree to within a specified value, typically 0.002 or 0.003 atomic mass units. This information constitutes the ELCOMP output.

The ELCOMP output listing normally includes 400 to 1000 lines detected in the spectrum, their intensities, and 500 to 2000 associated chemical composition data. The approach used for interpreting this large quantity of data was to sort the assigned elemental composition into classes according to heteroatom composition (i.e., C,H; C,H,O; C,H,N; C,H,S) and degree of hydrogen unsaturation indicated by rings and double bonds. The R + DB value provides a convenient means of organizing data into probable chemical compound categories. Some examples will illustrate this point:

TABLE 11. REPLICATE EXTRACTIONS AND LC SEPARATIONS ON A SITE SOIL SAMPLE

	% Water	Dry Wt. Extracted (kg)	Extract TCO (mg)	Extract GRAV (mg)	Extract Total (mg)	Total (mg/kg)
Before LC Fractionation						
Sample 1: APN 0-6	15.9	0.0966	ND	9.0	9.0	93.2
Sample 2: APN 0-6	15.6	0.1090	ND	8.0	8.0	73.4
After LC Fractionation						
Sample 1: APN 0-6						
LC-H			0.82	1.67	2.49	25.8
LC-A			0.39	1.17	1.56	16.1
LC-X			ND	4.00	4.00	41.4
						83.3
Sample 2: APN 0-6						
LC-H			ND	1.17	1.17	10.7
LC-A			1.30	0.50	1.70	15.6
LC-X			ND	5.30	5.30	48.6
						74.9

for an n-paraffin, C_6H_{14}, R + DB = 0

for phenol, C_6H_6O, R + DB = 4

for benzothiophene, C_6H_6S, R + DB = 6

for anthracene, $C_{14}H_{10}$, R + DB = 10

for benzopyrene, $C_{20}H_{12}$, R + DB = 15

All paraffins or other saturated species such as acyclic alcohols and sulfides will always be in R + DB group 0. A species must have an R + DB value of 4 or more to be aromatic, and R + DB value of 7 or more to be a naphthalene, an R + DB value of 8 or more to be a polychlorinated biphenyl (PCB), and so on. The R + DB values were grouped in this report as follows: R + DB = 0, 1 R + DB 4; 5 R + DB 9; 10 R + DB 14; and 15 R + DB.

Similar calculations can be made for any species of interest. This approach does not differentiate among the different isomers of any compound class, such as anthracene and phenanthrene, in R + DB 10.

The R + DB and elemental composition values were then used to sort all of the data from HRMS analysis into a compact matrix first according to the R + DB value and second according to the elemental composition of each of the ions identified. This approach presents a simple view of the overall composition of a sample from a highly complex spectrum. This approach requires that all ions finally included in the matrix are parent (molecular) ions. However, a large number of fragment ions in the spectra complicates the analysis. In interpreting the HRMS data it is also necessary to account for isotope ions (e.g., ^{13}C and ^{37}Cl), and composition assignments with large experimental errors. Consequently, in developing the R + DB matrix, certain restrictions were applied in an attempt to eliminate interferences and questionable calculated compositions. The restrictions applied were:

Molecular Weight: Ions below 90 atomix mass units were excluded to minimize the interference from fragment ions.

Error: Calculated compositions which differed from measured values by more than 2 millimass units were excluded.

Isotopes: All calculated compositions that included isotopes such as ^{13}C, ^{34}S, and ^{37}Cl were excluded.

R + DB: Only compositions with integral R + DB values were included, thus excluding fractional R + DB values which arise from fragment ions.

Carbon No.: A minimum carbon number limit was set for each R + DB class.

For this report, the individual intensities of all ions within each R + DB and element group were summed to give a single estimate of the abundance of that group. For each composite sample, these estimates were subsequently displayed in a condensed form as shown in Figure 9 .

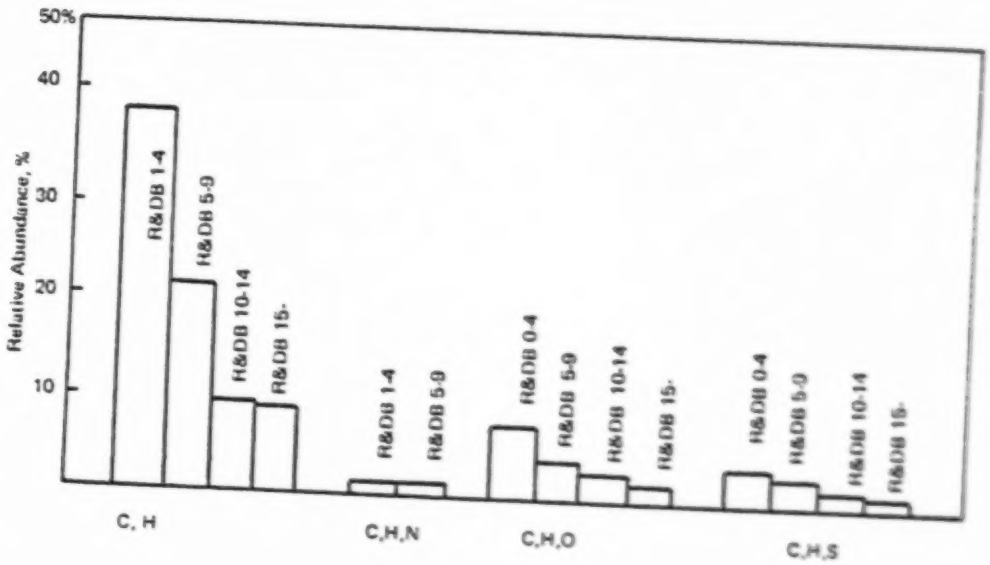

FIGURE 9. EXAMPLE OF DISPLAY OF R+DB AND ELEMENTAL COMPOSITION GROUPINGS FOR A SOIL SAMPLE EXTRACT